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E. A. Blum

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Contract Administrator

2410-2E2 (3rd Quarterly Report)

Third Quarterly Report

INVESTIGATION OF THE REINFORCEMENT OF DUCTILE METALS WITH STRONG, HIGH MODULUS DISCONTINUOUS, BRITTLE FIBERS

by

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prepared for

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SUMMARY

This program report covers the period 1 May 1967 to 31 July 1967; the work is being performed under Contract NASw-1543, with Mr. James J. Gangler of NASA-Headquarters serving as Program Monitor.

The purpose of this program is to define and investigate the critical factors affecting the reinforcement of ductile metals with short, brittle fibers. The materials systems selected for study are aluminum (or its alloys) and "ductile" epoxies reinforced with B_4C whiskers or with high modulus filaments, such as B_4C/B/W, SiC/W, B/W, etc. Related tasks in the program include the development of a more economical process for growing B_4C whiskers, deposition studies, the production of B_4C fibers, and the characterization of the individual constituents in the final composites. The latter task involves a study of the structural and chemical interactions of the combined elements (fibers, matrix, coatings, etc.).

The results obtained during this period are summarized as follows:

(1) The lack of success in consistently growing good quality B_4C whiskers by the BBr_3 t CCl_4 t H_2 system has been postulated as originating from the lack of nucleation due to the absence of B-C species. A new approach utilizing boron-carbon compounds which have B-C species in their deposition products is being studied as a possible solution to this problem.

(2) B_4C/B/W continuous filaments have been deposited on a large diameter B/W (.004" dia.) substrate, successfully at rates near 2 ft/min and at thicknesses up to .001" by the CCl_3 t CH_4 t H_2 process. Usually, no serious degradation of the properties of the original B/W material occurs. This has furnished a large supply of large diameter B_4C material, which is needed to continue continuous and discontinuous composite studies of both aluminum-based and epoxy-based materials.

(3) Previous results(1) had shown that metallic coatings of Ti/Ni on SiC/W and B_4C/B/W filaments are necessary to assure good wettability during aluminum infiltration of composites. Present studies confirm that Ti/Ni sputtered coatings on thermally cycled B_4C/B/W filament material do

not affect their room temperature tensile strength properties. Filaments so coated will be used for all subsequent aluminum-$B_4C/B/W$ composite studies. It is to be noted that such coatings on SiC/W filaments induced drastic changes in tensile properties resulting in the lowering of the strength of the material to near 25% of its former uncoated value.

(4) Results of studies to show the interaction effects of filaments in epoxy matrices are also presented. Interaction effects can profoundly affect the ability of the matrix to usefully redistribute stresses in composites having well-bonded brittle filaments.

(5) Preliminary results are also described which show that the individual characteristics of filaments can also affect the influence they exert on the composite and its matrix. As an example, B/W filaments processed so that their W cores retain their ductility do not show the characteristic 45° fracture pattern present in epoxy composites where the filament used is totally brittle.

(6) A theoretical study of the fracture patterns formed during tensile testing of epoxy filament composites show that these patterns are indeed an indication of the order in which filaments fail. These studies further lead to the postulation that modifications of the matrix characteristics and interfacial bonding between the phases can be controlled to provide a more efficient reinforced material.

I. INTRODUCTION

From a reinforcing viewpoint, whiskers (single-crystal filaments) appear to have many desirable characteristics. A number of classes of compounds have been prepared in this form including metals, oxides, nitrides, carbides, and graphite. The maximum strengths observed for these whiskers range from about 0.05 to 0.1 of their elastic moduli, approaching predicted theoretical strengths. Many also have relatively low densities and are stable at high temperatures. Calculations of whisker-reinforced composite properties based on whisker properties, particularly for the brittle whiskers of high modulus materials, show that they have enormous potential compared to more conventional materials on both a strength/density and a modulus/density basis.

The incorporation of whiskers into composites requires the following series of processing steps:

1) Whisker growth
2) Whisker beneficiation, to separate strong fibers from the growth debris
3) Whisker classification, to separate according to size
4) Whisker orientation, to align the whiskers and maximize reinforcement along a specific axis
5) Whisker coating, to promote wetting and bonding
6) Whisker impregnation with matrix material, to form a sound strong composite.

Because of the many processing steps, there is a large number of imposing technical problems to be solved in order to achieve the high potential strengths. Many of these problems have not yet been solved.

In a few isolated cases, involving very small and carefully prepared samples, the predicted strengths of the brittle whisker/ductile matrix composites have been achieved. However, all too frequently, attempts to scale up the composites into even modest size specimens have resulted in strengths that range from about 10 to 30 per cent of the predicted values.

A list of possible reasons for the low composite strength values is given in Table I. As can be seen, there are many variables to contend with, and many of these are interrelated and difficult to study experimentally.

TABLE I. VARIABLES AFFECTING THE TENSILE STRENGTH OF WHISKER-REINFORCED COMPOSITES

A. Whisker Variables

1, Average strength

2, Dispersion of strength values

3. Strength versus whisker diameter and length

4. Strength degradation during handling and fabrication

5. Strength versus temperature

6. Modulus

B. Matrix Variables

7. Yield strength

8. Flow properties

9. Strength versus temperature (particularly shear strength)

10. Matrix embrittlement due to mechanical constraints on new phases formed

C. Composite Variables

11. Volume fractions of components--fiber and matrix

12. Homogeneity of whisker distribution

A fundamental difficulty in evaluating the performance of whisker composites is the lack of knowledge concerning the whiskers themselves. This is understandable when one realizes that there are about 10^9 to 10^{10} of them per pound, and characterization of even a small fraction becomes a major task. These and other problems have limited the immediate use of B_4C whiskers, which are synthesized and characterized in previous studies (3, 4, 5, 6).

An alternate means to gain useful, fundamental knowledge concerning whisker-reinforced composites involves the use of brittle, continuous filaments. Continuous filaments have several advantages over whiskers when investigating the reinforcement of materials; some of these advantages are listed below:

1) It is much easier to characterize the relevant and critical parameters listed in Table I.
2) The available continuous filaments are large relative to the whiskers and can be more readily handled and incorporated into composites.
3) The filaments can be cut to uniform, desired lengths of symmetrical geometry so that the effects of discontinuous reinforcements can be assessed.

Experimental work of this type has already been done using ductile filaments such as tungsten in a ductile matrix such as copper[2]. Although this work has provided a wealth of information regarding the reinforcement of metals, it does not uncover all of the key problems encountered in the brittle fiber/ductile matrix systems which are potentially of great technological importance. The chief difference between the reinforcement of metals with brittle and ductile fibers is that ductile fibers can deform to accommodate local, high stress concentrations, whereas brittle fibers cannot do so. Thus, it is necessary to carry out further studies and to evaluate the potential and engineering limitations of metals reinforced with brittle fibers and whiskers.

This program was therefore initiated to investigate in detail the behavior of a ductile metal (aluminum) reinforced with various brittle fibers, such as $B_4C/B/W$, SiC/W, B/W, etc. (both continuous and chopped), to provide data which would be pertinent to whisker-reinforced metals. This program is being conducted in two parts: (1) development of a process to grow B_4C whiskers which would be amenable to eventual scale-up, and (2) to investigate the reinforcement of aluminum with brittle, high modulus filaments. When sufficient quantities of whiskers become available, they will be used in the composite studies also.

During the third quarter the method of producing B_4C whiskers has been modified. Useful quantities of $B_4C/B/W$ continuous filament have been produced by the process developed during the second quarter. Considerable effort has been directed toward understanding the relationship between the phenomenology of fracture and the mechanical behavior of composites. The understanding gained thus far is to be evaluated with the aim of early publication.

II. EXPERIMENTAL PROCEDURES--RESULTS AND DISCUSSION

A, BORON CARBIDE FILAMENT DEPOSITION AND WHISKER-GROWTH STUDIES

1. Boron Carbide Continuous Filaments

As discussed in a previous report[1,6] boron carbide coatings can be deposited on continuous boron filaments having a tungsten substrate without seriously affecting the tensile strength of the starting filament. This technique permits the rapid preparation of $B_4C/B/W$ filaments of significant diameter (i.e., ~4 mils) for use in subsequent composite studies. The direct deposition of boron carbide on a tungsten substrate, while feasible, is considerably slower and yields a product of smaller diameter and inferior properties.

During the recent report period, a series of boron carbide depositions was made on 4-mil boron/W substrate at various filament draw speeds to obtain boron carbide coatings of varying thickness. Table II summarizes the results which indicate that, although in some cases the initial tensile strength of the boron substrate was either unaffected or was restored, in other cases serious losses in strength were encountered. At present, it can only be speculated that slight variations above the desired deposition temperature of boron carbide may have caused great damage to the filament, which itself had been prepared at a similar temperature.

The surface appearance of these various deposits was the same as that of the first deposits described in an earlier report with the exception that the thinnest coating permits the nodules of the boron substrate to show through (see Figures 1 and 2).

Further work will be carried out using a somewhat stronger starting boron filament, while keeping deposition temperatures as low as is commensurate with a reasonable (.3-.5 mils) radius thickness.

2. Boron Carbide Whisker-Growth Studies

a. Boron and Carbon Halide Feed Mixtures

Since the start of the program, efforts have been directed toward developing a method for growing boron carbide whiskers which would be more economical and somewhat more amenable to continuous production than the evaporation method used earlier. Thermodynamic calculations presented in a

TABLE II

Speed ft/min	Tensile Strength, ksi Avg.	High	Low	Modulus 10^6 psi	Thickness (mils on radius)	Total Dia. mils
1.08	209	231	186	61	0.5	5.0
1.08	101	132	80	52	0.65	5.3
2.16	36	86	5	40	0.5	5.0
3.24	119	156	101	64	0.4	4.8
9.72	232	266	120	52	0. 15	4.3

initial B/W Strength = 241 ksi; B/W Strength after Heating = 104 ksi.

previous report (Ref.6) indicated that the necessary but not sufficient condition of generating reduced boron and carbon species in the vapor phase could be accomplished by heating a dilute mixture of boron tribromide (BBr_3) and carbon tetrachloride (CCl_4) vapors in hydrogen to temperatures around 1400°C.

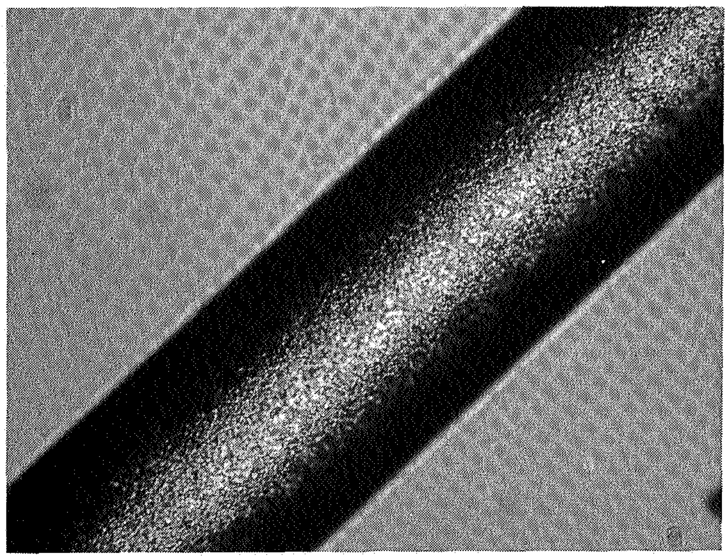


Figure 1. B_4C Coating on B/W Filament Substrate Coating is 0.4 Mils Thick on Radius (240X)

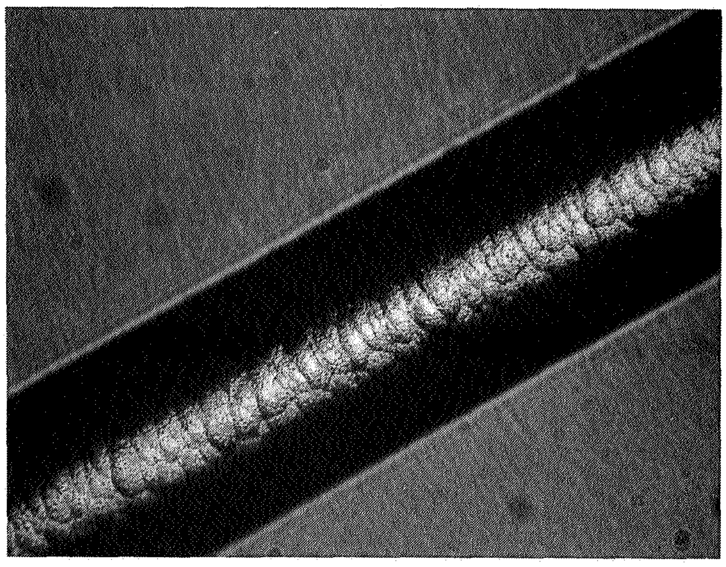


Figure 2. B_4C Coating on B/W Filament Substrate Coating is 0.15 Mils Thick on Radius (240X)

The experimental arrangement shown in Figure 3 was used to carry out a number of exploratory runs to delineate what conditions of concentration, flow and pressure would be most likely to yield whiskers by this method, always assuming, of course, that nucleation could occur in this environment and with the available boron and carbon species. {The system was operated at a given pressure by balancing the feed rate versus exhaust rate to maintain constant pressure.) To assist in generation of nuclei, vanadium tetrachloride was added to the feed mixture in certain runs, while in others, vanadium metal and impure boron carbide were placed in the growth zone. Addition of these ingredients was based on the earlier work of Gatti et al[3] which indicated the effectiveness of vanadium as well as other compounds of impure boron carbide as thin layers or as chunky or dendritic massive crystals. In the few cases where whiskers formed, they were short and heavily overgrown (see Figure 4). The appearance of these whiskers is believed to have been due to prior "seeding" treatments. The course of events might be described as having consisted of evaporation of boron carbide during the seeding treatment, with deposition of

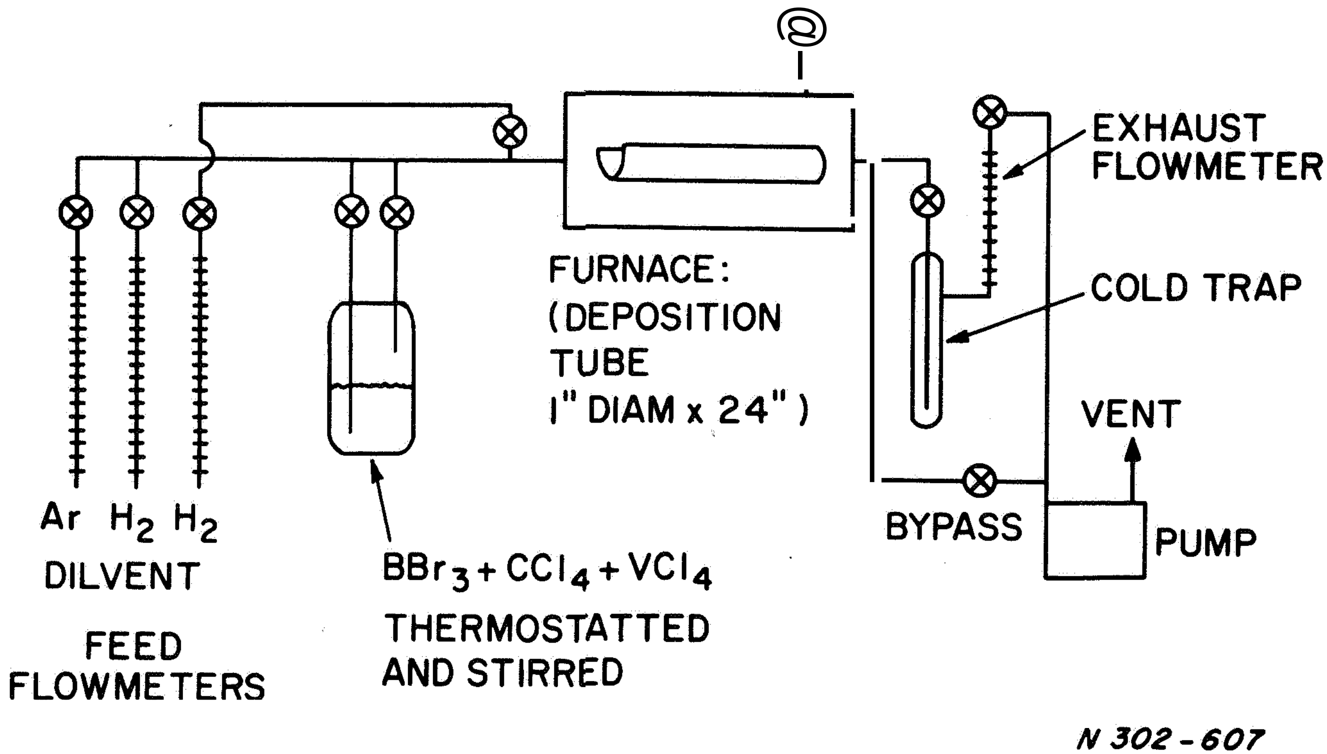
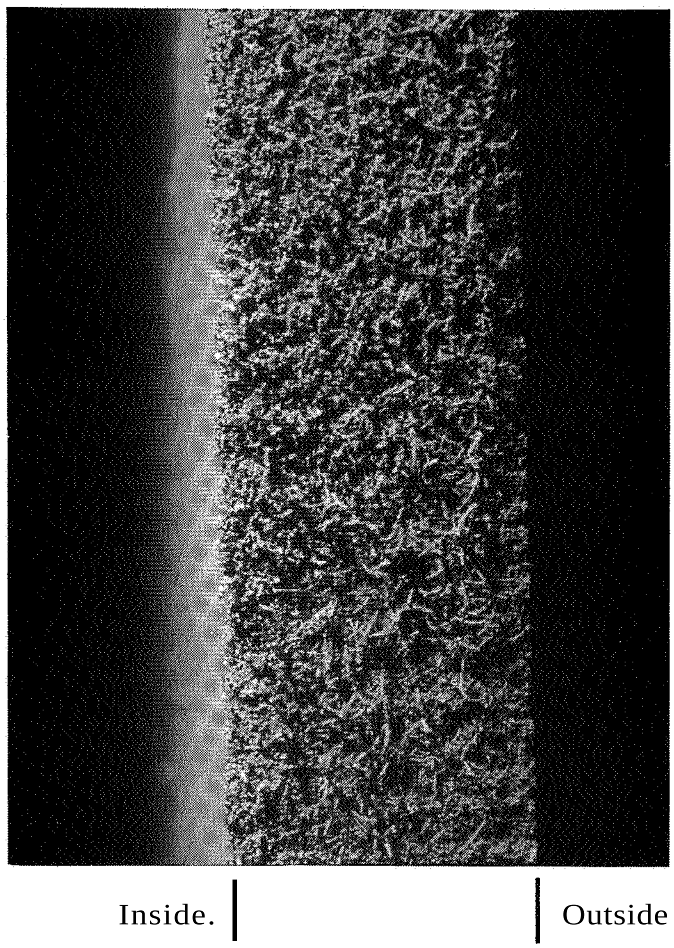


Figure 3. Flow System for sker Growth by Reduction of BBr_3 +CC $_4$



Upstream Right Edge of Tube
$\sim 8^{\circ}$ From Inlet

Figure **4.** B_4C Whisker Cluster (Run 61-13-11D, 10X) potential nucleating species on the furnace element, followed by re-evaporation of the nucleating species during the subsequent halide run and redeposition in the furnace tube. The deposit formed from the species originating from the halide mixture served mostly to produce the layer deposit and overgrowths.

Table III presents the experimental data and results. The experimental conditions, aside from temperature, are summed up in the "flux" term, after Noone and Roberts[4], which is defined as the product of gas phase concentration of the halide feed and the velocity of the gas through the furnace. This term thus includes less clear concepts such as collision number and efficiency, side reactions etc. which are functions of time and concentration. If a critical flux value exists which separates the area of concentration and velocity variation into regions in which whiskers or plate deposits predominate, this should appear as a dividing line between the region in *a* plot of concentration versus velocity. Such a plot shows no such clear division, however.

Part of the explanation for the absence of whisker deposits in the process explored thus far may lie in the nature of the vapor species. Evaporation of boron carbide, while it yields boron as the predominant specie, also produces BC, B_2C and BC_2[5] species which may be required for nucleation if not actual growth. On the other hand, reduction or decomposition of boron tribromide and carbon tetrachloride undoubtedly produces boron and carbon, which if they exceed supersaturation, will deposit and then form boron carbide of uncertain stoichiometry. This is no doubt the origin of the plate-like deposits. However, since the likelihood of formation of polynuclear species is slight, whisker formation is negligible.

Other methods are available for introducing boron and carbon species into the gas phase, polyatomic as well as monatomic. These include the use of various volatile substituted boranes such as tributyl borane ($B(C_4H_9)_3$) and ethyl decaborane ($C_2H_5B_{10}H_{13}$). Experiments are now in progress to evaluate these as feed materials which may be more likely to provide the required species to nucleate whisker formation.

TABLE III. EXPERIMENTAL DATA FOR WHISKER-GROWTH RUNS

H_2 Flow cc/min. Through Halide	Total H_2 Flow to furnace	Percent Halide in Feed	Gas Velocity cc/min.	Flux	Total Press.	Temp. °C	Result
23	23	2.80	1.9	5.3	760	1400	W
15	15	2.80	1.3	3.5	760	1400	--
23	23	2.80	1.9	5.3	700	1380	--
50	50	11.00	4.2	46.0	720	1520	--
58	105	1.70	8.8	15.0	760	1400	P
42	42	2.80	3.5	10.0	730	1440	P
42	42	2.80	3.5	10.0	740	1330	P
75	150	5.50	12.6	70.0	760	1590	P
19	134	0.40	11.3	4.5	760	1400	P
73	73	3.20	6.2	19.0	770	1440	--
20	20	3.20	1.7	5.0	700	1400	--
40	40	12.30	3.4	4.0	720	1490	wh
36	76	5.80	6.4	37.0	710	1480	P
42	42	20.00	3.5	71.0	120	1490	P
11	11	3.30	1.0	3.0	720	1600	P
50	50	0.70	4.2	3.0	740	1500	wh
2	2	2.60	0.4	1.0	190	1500	P
2	2	0.70	0.2	0.1	700	1400	P

Results - Some whiskers or whisker-like deposits: W
Plate deposit: P
Abortive run, leaked etc.: --

Time = 4 hours.

B. $B_4C/B/W$ FILAMENT CHARACTERIZATION STUDIES

Studies of continuous filament composites of Al-$B_4C/B/W$[5] had shown that efficient reinforcement was possible, at least with the approximately 40 volume percent filaments then used. A more extensive program was initiated using SiC/W filaments in an attempt to more fully study the continuous reinforcement of aluminum as a function of volume fraction. The decision to use SiC/W filaments was made to simplify the handling of large quantities of filament, because the $B_4C/B/W$ filaments then on hand were less than 0.0027" in diameter, while the SiC/W filaments averaged 0.004" in diameter. (It is to be noted that this supply problem of large diameter $B_4C/B/W$ material has been solved.) Accordingly, a large number of 2" long, 0.004"-diameter SiC/W filaments were cut for use in a liquid aluminum infiltration apparatus. Ti/Ni coatings were found necessary to promote wetting in order for complete infiltration to take place''). Tensile test results of the infiltrated composites showed that these composites were only 25% as strong in tension as their potential strength calculated by the rule of mixtures. Further studies on the effect of Ti coatings on the strength of SiC/W filaments was subsequently made and it was shown that the filaments were being weakened due to the mobility of silicon in the presence of Titanium''). Similar electron probe studies on Ti/Ni coated $B_4C/B/W$ filaments showed no reactions[6] leading to the speculation that the coatings were thus not affecting the strength of the $B_4C/B/W$ filaments. In order to clarify this point, before extensive composite studies were begun, experiments similar to those performed on the Ti/Ni coated SiC/W filaments were made viz. Ti/Ni coated $B_4C/B/W$ material was thermally cycled under infiltrating conditions of temperature, atmosphere, and time and then tested for strength changes. Figure 5 shows the results of these experiments. Included in the figure are the previous results obtained on SiC/W for comparison purposes. It is to be seen that although a sharp change in tensile properties is noted for the SiC/W coated material, essentially no change in properties was measured for the Ti/Ni coated $B_4C/B/W$ material. The

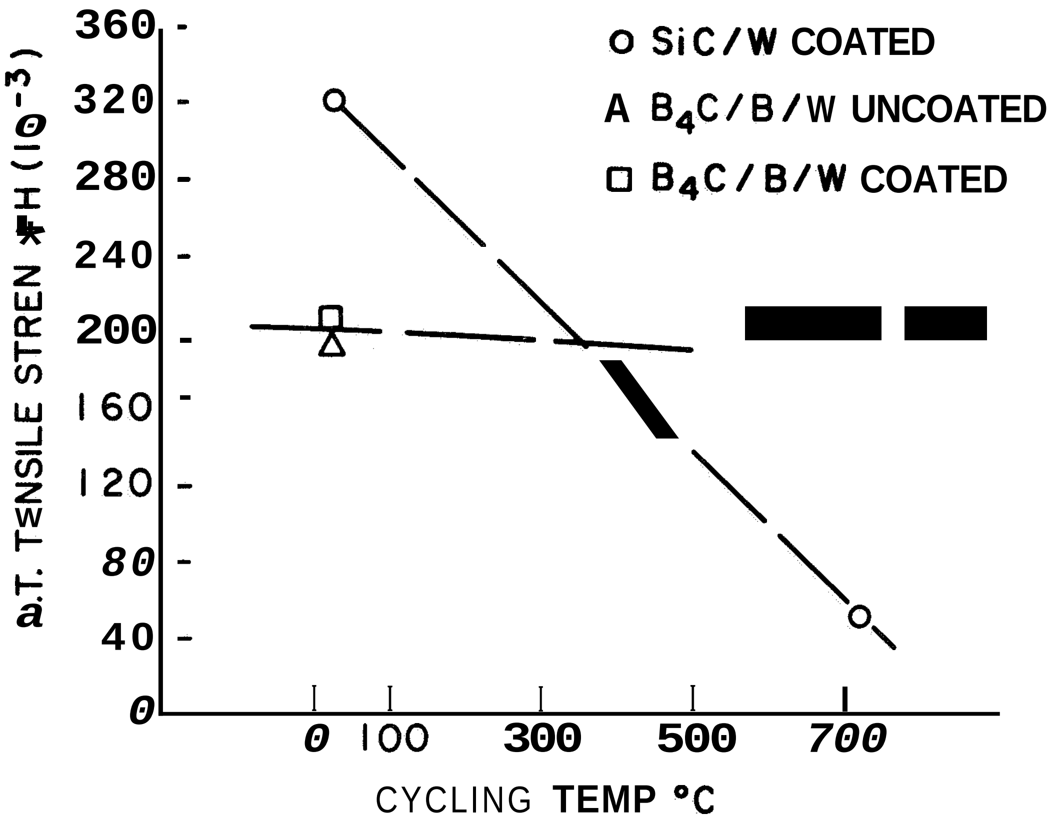


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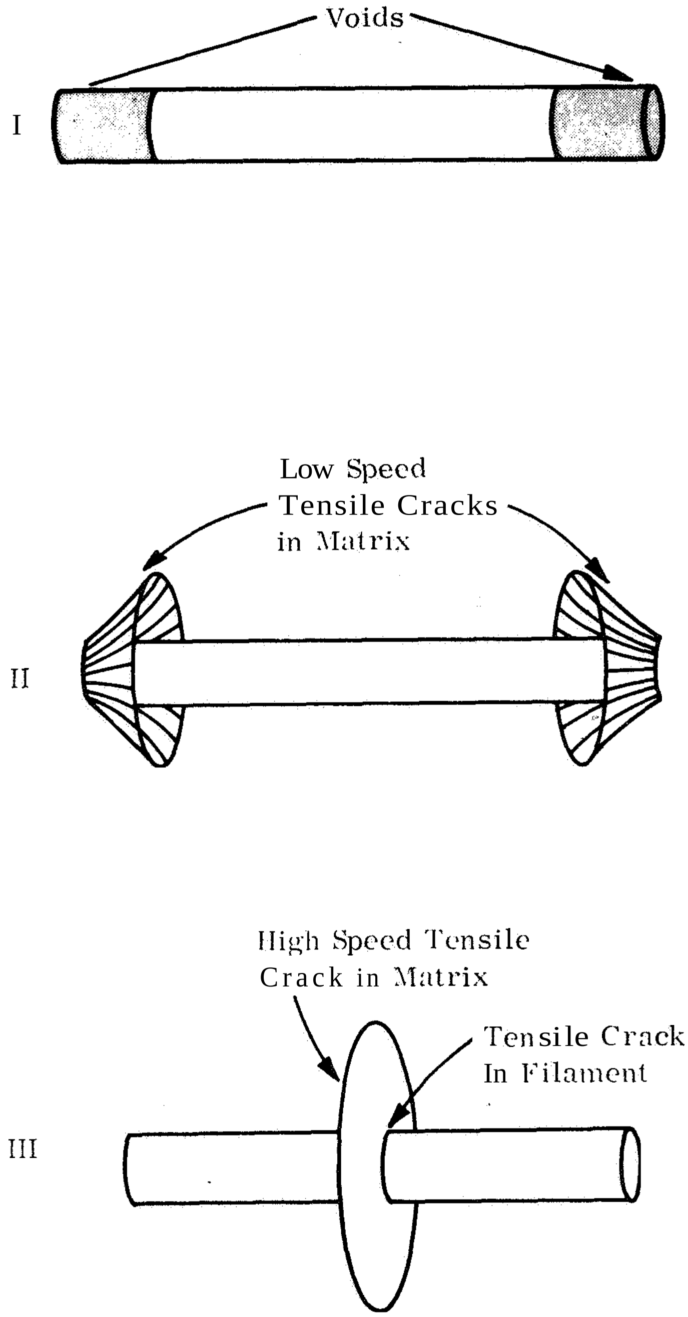
Figure 5. Effect of Thermal Cycling on the Average Room Temperature Tensile Strength of Ti/Ni Coated SiC/W and $B_4C/B/W$ Filaments

results thus obtained give added confidence that $B_4C/B/W$ filaments are ideal for aluminum-based composite materials and are capable of maintaining their chemical and mechanical stability at high temperatures.

C. COMPOSITE STUDIES, EPOXY-FIBER MATERIALS

The significance of the current studies on single and multiple-filament epoxy matrix composites (tested in tension) is that at least three failure modes are possible. Normally, two have been considered previously. These modes are schematically represented in Figure 6. Modes I and II depict bond failure and matrix tensile failure at the ends of a filament, but each failure mode can also arise after a low-energy filament failure provides freely formed ends. Modes I and II require some time for composite failure to develop. Mode III involves a high speed tensile crack in the matrix, and it sometimes has a dynamically catastrophic effect upon nearby filaments in a multiple filament composite. Specimens frequently exhibit mixed failure modes, but it is unusual for Modes I and II to appear in the same specimen. Further consideration of the failure modes of composite materials are presented in Section IID of this report.



I. Interface or Matrix Failure in Shear Associated with Weak Bonding, Low Shear Strength Matrix Low Strain Rate or High Filament Strength.

II. Tensile Failure in Matrix Under Resolved Tensile Component of Shear Stresses at End of Filament. Associated with Low Tensile Strength Matrix (Relative to the Bond Shear Strength). High Tensile Strength Filament and/or Low Strain Rate.

III. Tensile Failure in Matrix Originating at Tensile Crack in Filament. Associated with Good Bonding. High Filament Strength and/or High Strain Rate.

Figure 6. Failure Modes in Fiber Composites

The work on filament-epoxy composites has been expanded to include different filaments and some effects of filament interaction on fracture mode. An analytical description has been developed to rationalize some of the fracture phenomena observed in single filament-epoxy composites, and it is also presented in Section IID.

Figure 7 is a schematic representation of some results obtained during tensile tests on single and multiple filament epoxy composites having very good bonding. Neither kind of specimen can be considered to be "reinforced" because of the very low fiber concentration. The five element specimens have a fiber volume fraction of about 0.1% and an interfilament spacing of 0.025 inch (i.e, 6 filament diameters apart). Nevertheless, some profound differences associated with filament interaction effects were apparent. The number of breaks per filament (prior to specimen fracture) was nearly independent of strain rate in single filament specimens but was markedly strain-rate dependent for the five-filament specimens. At the same strain rate, the multiple filament composite exhibited only about one-half the number of breaks per filament exhibited by the single filament specimen. The five-filament composite, strained at the lower rate, exhibited approximately twice the strength and ten times the elongation-to-failure exhibited by the specimen tested at the higher strain rate.

These results indicate that interaction effects can profoundly affect the ability of the matrix to usefully redistribute stresses in composites having well bonded brittle filaments. While epoxies are notoriously strain-rate sensitive and tend to be brittle, the possibility of analogous behavior (low strength brittleness) at high volume fractions in metal matrices cannot be ignored.

In addition to the work described above, some additional results were obtained using other filaments. All the results are summarized in Table IV for convenience in comparison. The B/SiO_2 filaments exhibited a larger number of breaks, under comparable conditions, than the $B_4C/B/W$ filaments. The difference is consistent with the difference in the strength of the filaments

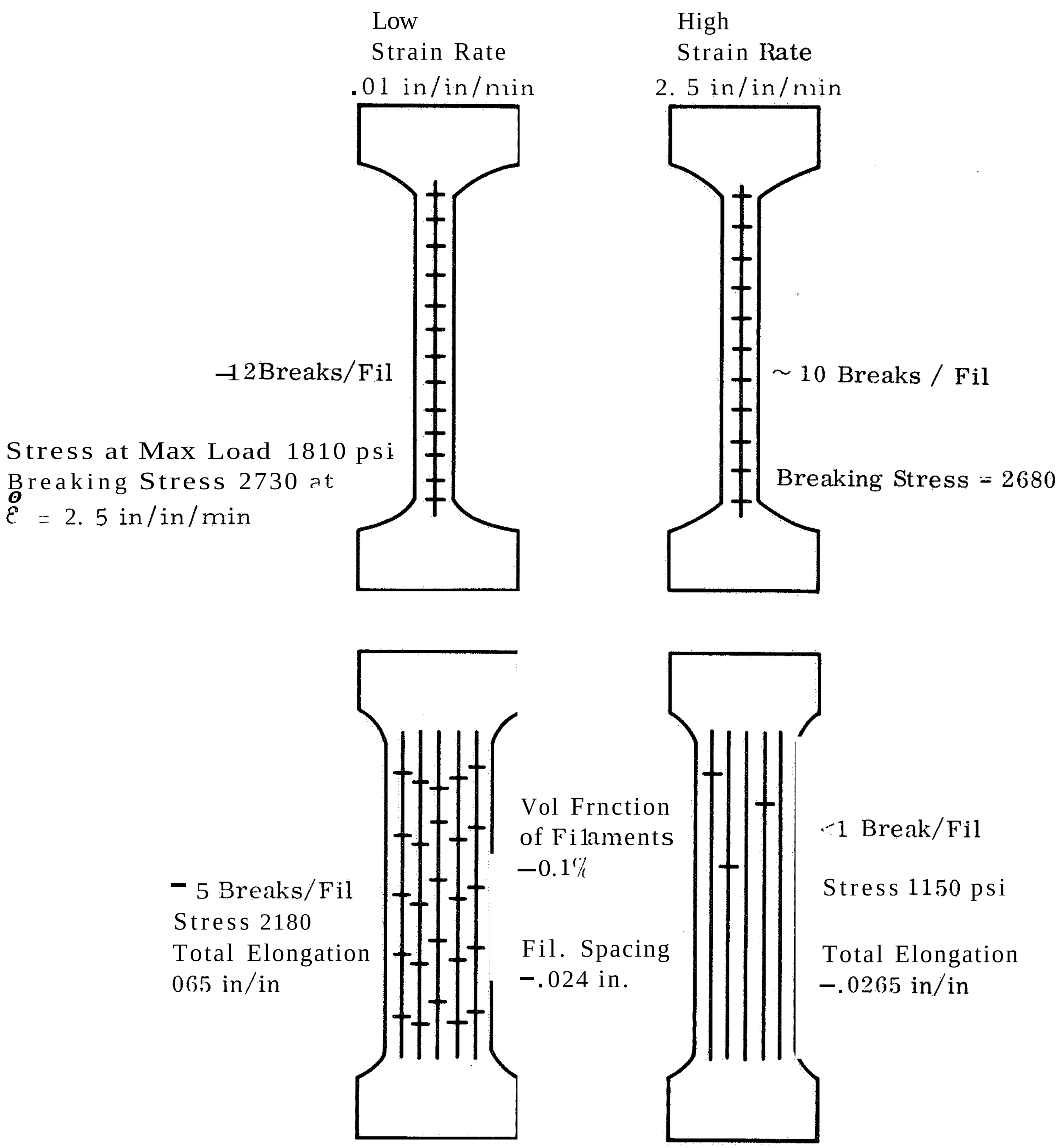


Figure 7. The Effect of Strain Rate and Filament Spacing on the Number of Breaks/Filament

($B_4C/B/W$ being the stronger). A special run of boron filament was made on a tungsten substrate at a temperature too low for substrate reaction. This filament is very weak in that the boron breaks very easily but it retains its integrity because of the strength of the unreacted (and ductile) substrate. As indicated in Table IV, this filament exhibited many more breaks than the other filaments. However, even at the lower strain rate, none of the (initially 45°) slowly growing cracks in the matrix (mode 11, Figure 6) occurred near filament tensile breaks. This probably indicates that the tungsten core (rather than the adjacent matrix) is carrying the extra load imposed by the failure of the boron sheath. This difference in fracture mode indicates that the introduction of some ductility in the filament may have profound effect on composite performance.

D. SOME THEORETICAL CONSIDERATIONS OF COMPOSITE FRACTURE

1. Fracture of Matrix in Single Filament Composites

From observations of fractures in single filaments imbedded in an epoxy matrix, certain phenomena appear to indicate that two modes of matrix tensile fracture are possible. To describe these mechanisms the following model is proposed:

Consider a single filament of length 1, loaded through shear at the interface as shown in Figure 8. The normal stress in the filament is induced

TABLE IV. NUMBER OF BREAKS/2" FILAMENT LENGTH AT INDICATED NOMINAL STRAIN RATE OF VARIOUS FILAMENT MATERIALS

Filament Type and Specimen Configuration	0.01 in/in/min	2.5 in/in/min
$B_4C/B/W$ - single filament	12	10
B/SO_2 - single filament	15	11
$B_4C/B/W$ - 5 filament	5	1
B/SiO_2 - 5 filament	9	--
B/W - 2 filament*	32	21
$B_4C/B/W$ - 2 filament*	10	10

*A single specimen containing 1 $B_4C/B/W$ filament and one boron filament made at a temperature less than that required to react the tungsten substrate.

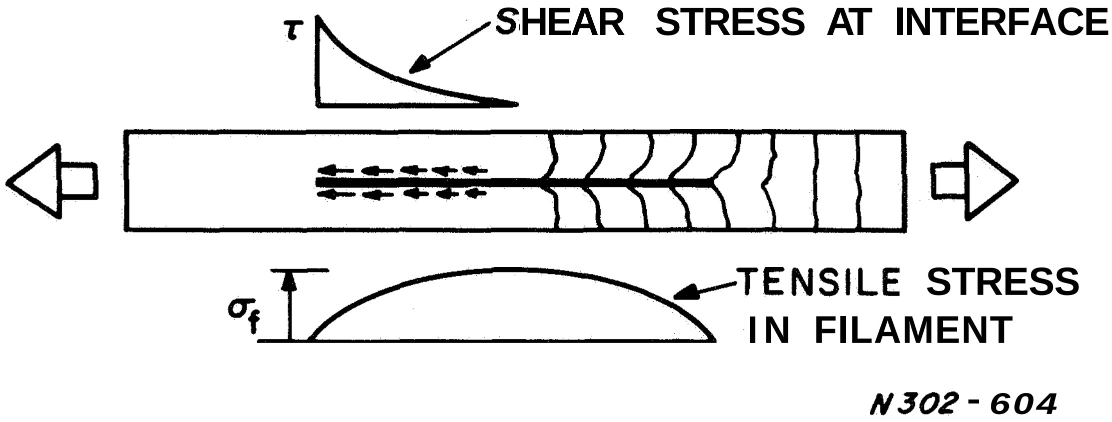


Figure 8. Schematic Representation of a Single Filament in a Composite Loaded Through Shear

by shear at the interface arising from the difference in modulus of the matrix and filament. The relation between the filament tensile stress and the shear at the interface can be developed from equilibrium of a segment of filament,

$$\frac{d\sigma_f}{dz} = \frac{4\tau}{d} \tag{1}$$

where z is the length along the filament and d is its diameter. Studies by Shuster and Scala[7] and Tyson and Davies[8] employed photoelasticity to describe the stress state in the matrix surrounding the filament. The latter study was done on a 4 mm diameter dural bar in Araldite CT 200 and gives variation in the matrix shear stress with radial distance from the filament end as shown in Figure 9. Note that the presence of the filament in the matrix is only felt at radial distances below two filament diameters. (Beyond this distance, the maximum shear stress in the matrix is half the applied tensile stress, σ_m as in an unreinforced specimen.)

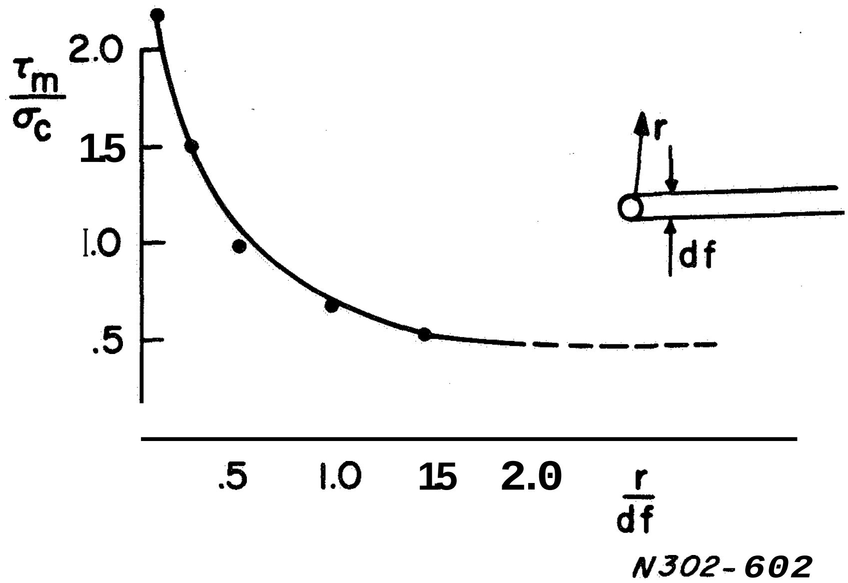


Figure 9. Shear Stress Variation Radial to Filament after Tyson and Davies[8]

If the ratio of the maximum shear stress in the presence of a filament to that of the unreinforced matrix is considered a stress concentration factor, it can be shown that the factor reaches a maximum of about 2 to 2.5 near the end of the filament.

2. Stress State and Its Relation to the Fracture Process

The source of the matrix crack in the absence of external notches and abrasions is the fracture of the filament at some critical stress level. Since the matrix is subjected to a characteristic stress state at the time of this fracture, it is important to determine how this stress state influences the fracture process. The normal stress trajectories in the matrix are sketched in Figure 10. The element A has very nearly a zero stress state since it is near the center of the filament where there is very little stress transfer from matrix to filament and the filament is carrying maximum tensile stress. When the filament fractures near its center, the matrix element A is suddenly subjected to a tensile stress in the direction of the filament axis. Fracture then occurs normal to this direction as a disk shape

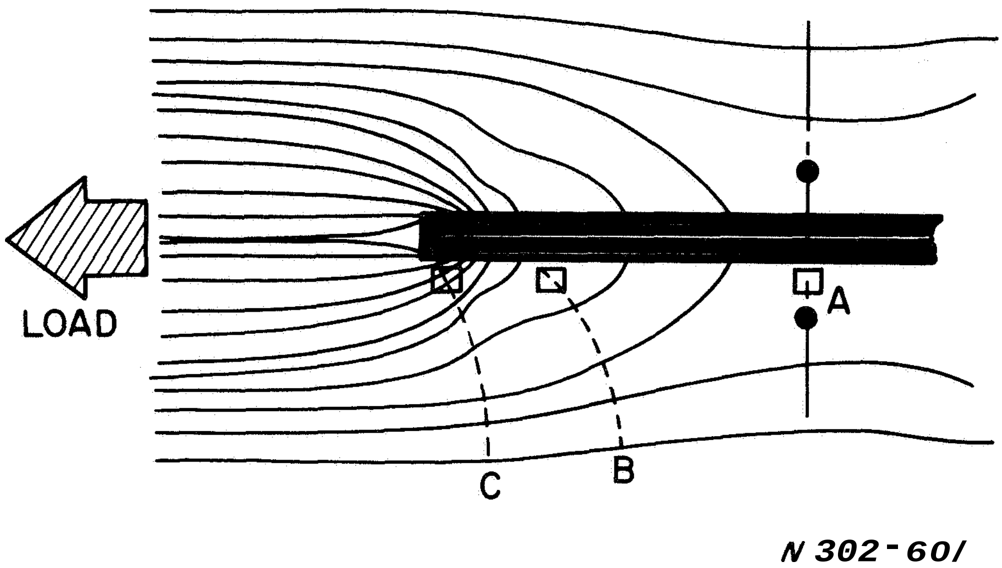


Figure 10. Stress Trajectories for Normal Stress in Matrix

is formed which may continue to propagate or may stop as shown in Figure 11. (Also, see Figures 6 and 12.) The governing factor in stopping the crack is the ability of the matrix to dissipate the initial energy input from the filament fracture as the disk grows. This phenomenon has been observed in many cases as shown in Figures 12A and 12B. When the matrix cracks near the end of a filament, the fracture pattern is quite different because of the stress state. Consider the failure of the matrix at element B (see Figure 10) which is near the end of the filament (which may have been formed by a previous filament break). According to the stress state described by Tyson and Davies[8], this element is subjected to shear and normal stresses with the shear stresses at the interface reaching 1.25 times the gross composite tensile stress σ_c. When the shear stress at the interface is large compared to the normal stress, as in element B, a state of stress approximating pure shear results and the critical tensile stress is at 45^o to the filament as shown in Figure 13. This results in a cone shaped crack also shown in Figure 13.

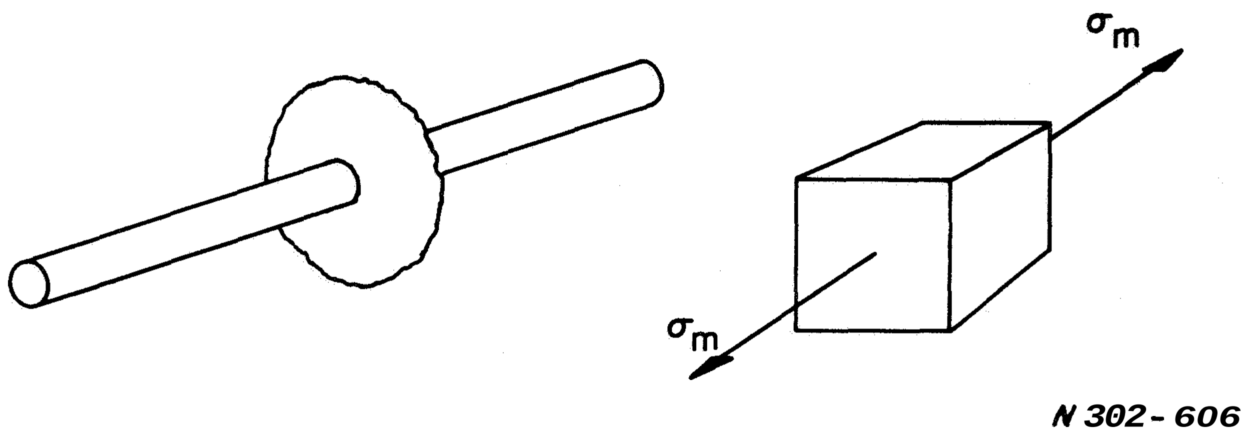
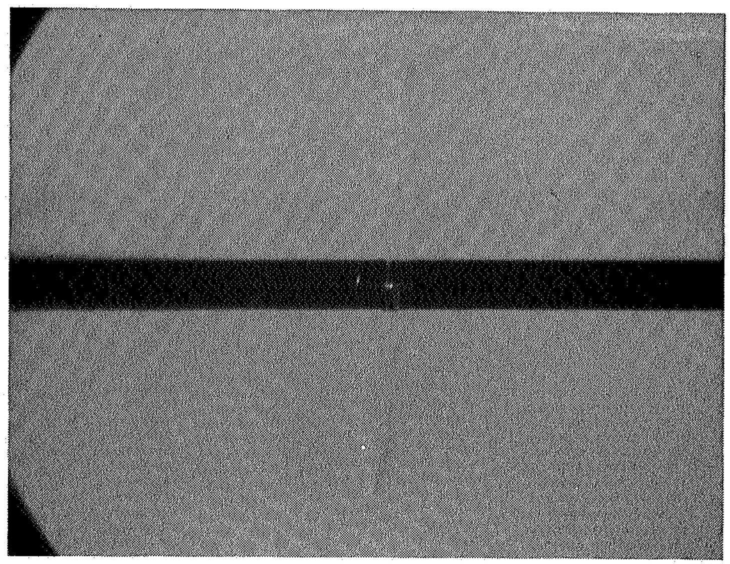
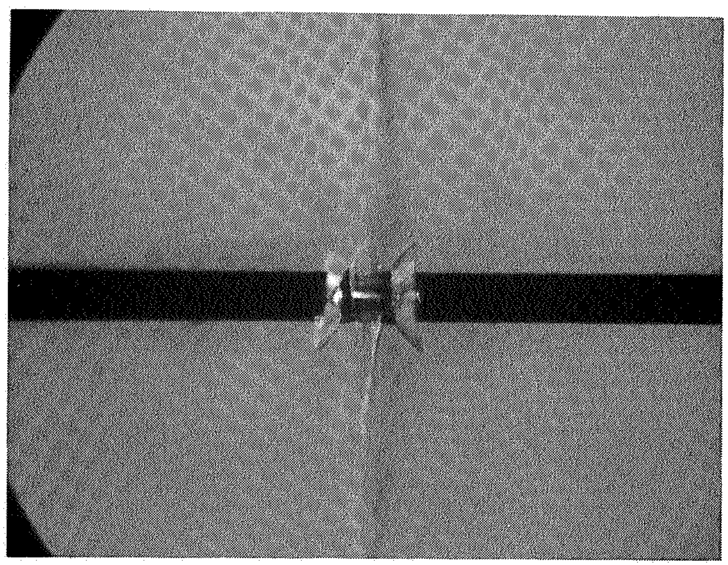


Figure 11. Disk-Shaped Cracks and Stress State in the Matrix

Nearer to the end of the filament, a similar crack is initiated but'the angle of inclination to the filament is greater since the stress state is not pure shear at the filament ends. Some normal stress exists and the end geometry introduces some discontinuity in the shear transfer mechanism. As the crack propagates, it follows a path normal to the tensile stress trajectories inthe matrix until it becomes normal to the filament and is outside the range of influence of the reinforcing filament. This is illustrated in Figure 14. When a filament fractures at very low load levels (because of a weak spot e. g.) the fracture of the filament is not accompanied by a disk shaped matrix crack as shown in Figure 15. As the load is increased, the cone shaped fractures just described will propagate from the newly formed ends, if the specimen does not fail first. Plotting the locus of the crack in Figure 14 against the maximum normal stress planes at a corresponding distance from the filament end we obtain the plot shown in Figure 16.



A. Low Total Strain



B. Higher Total Strain

Figure 12. Examples of Disk-Shaped Cracks in Epoxy-Filament Composites Which Have Stopped - 56X

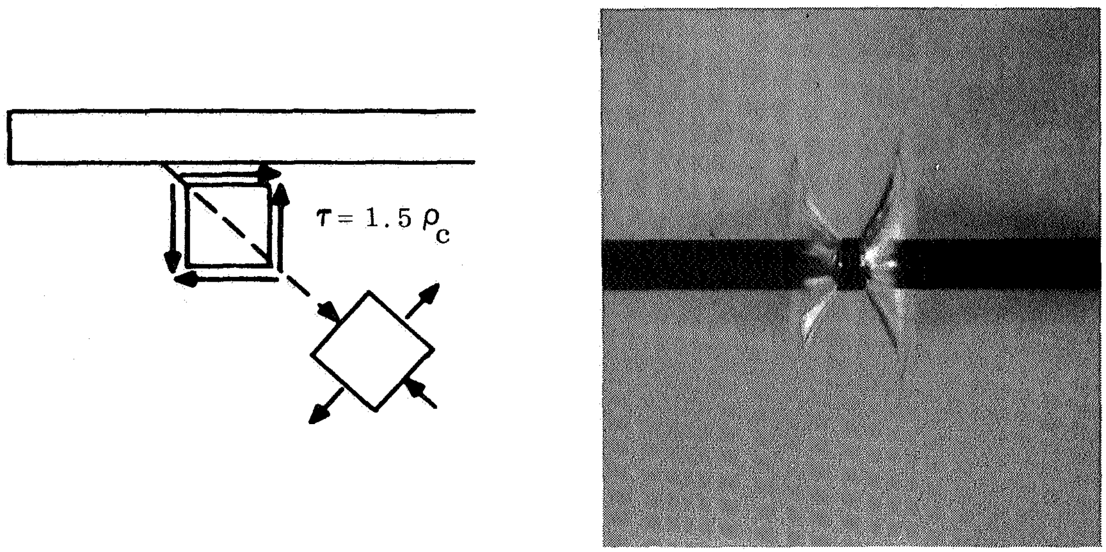


Figure 13. Schematic Representation of Stress Distribution at Filament End and Photograph of Resulting Cone Type Crack Which Results - 56X

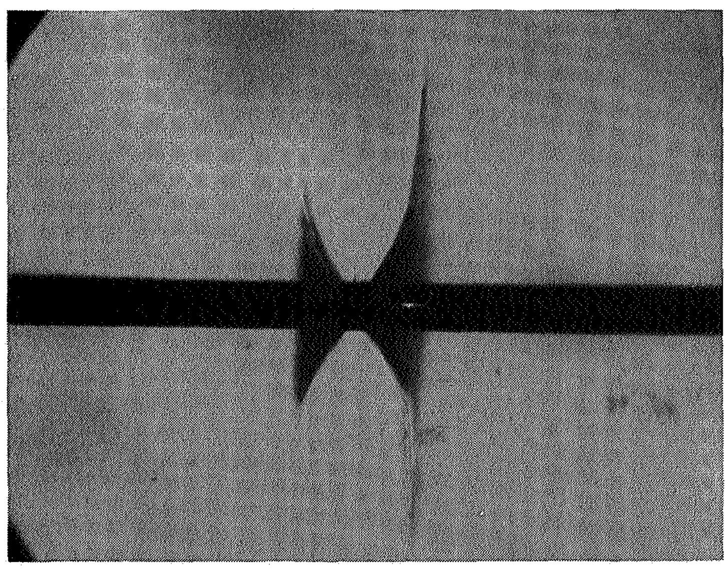


Figure 14. Photograph of $B_4C/B/W$ Filament in Epoxy Illustrating Crack Propagation Which Follows Path Normal to Tensile Stress Trajectories - 56X

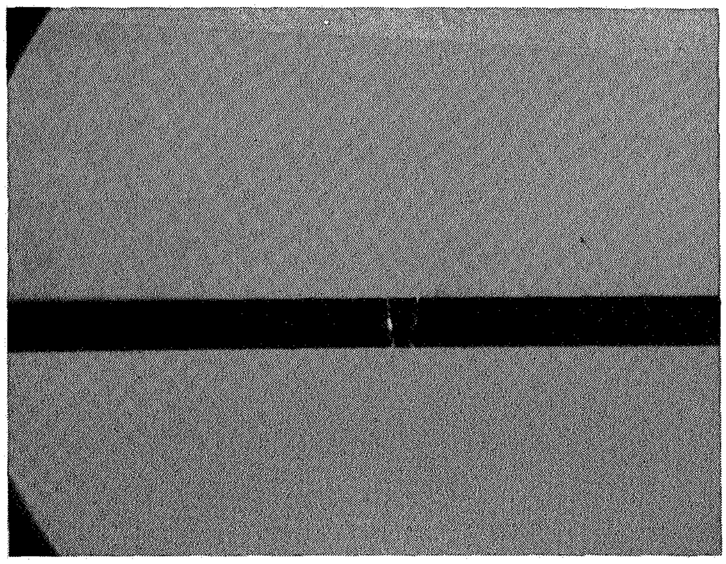


Figure 15. Photograph of Broken Filament with No Crack in Matrix - 56X

The figure shows reasonably good agreement between the crack path and the locus of the planes of maximum normal stress in the matrix. From this limited data, it is quite obvious that the analysis of the stress state in the matrix is a necessary and useful tool in understanding the fracture process. Since the local stress state varies considerably along a given filament during the failure process, the fracture patterns are a valuable indication of the order in which filaments break. Further, by modifying the matrix characteristics and interface bond, the failure process can be controlled to provide a more efficient reinforced material.

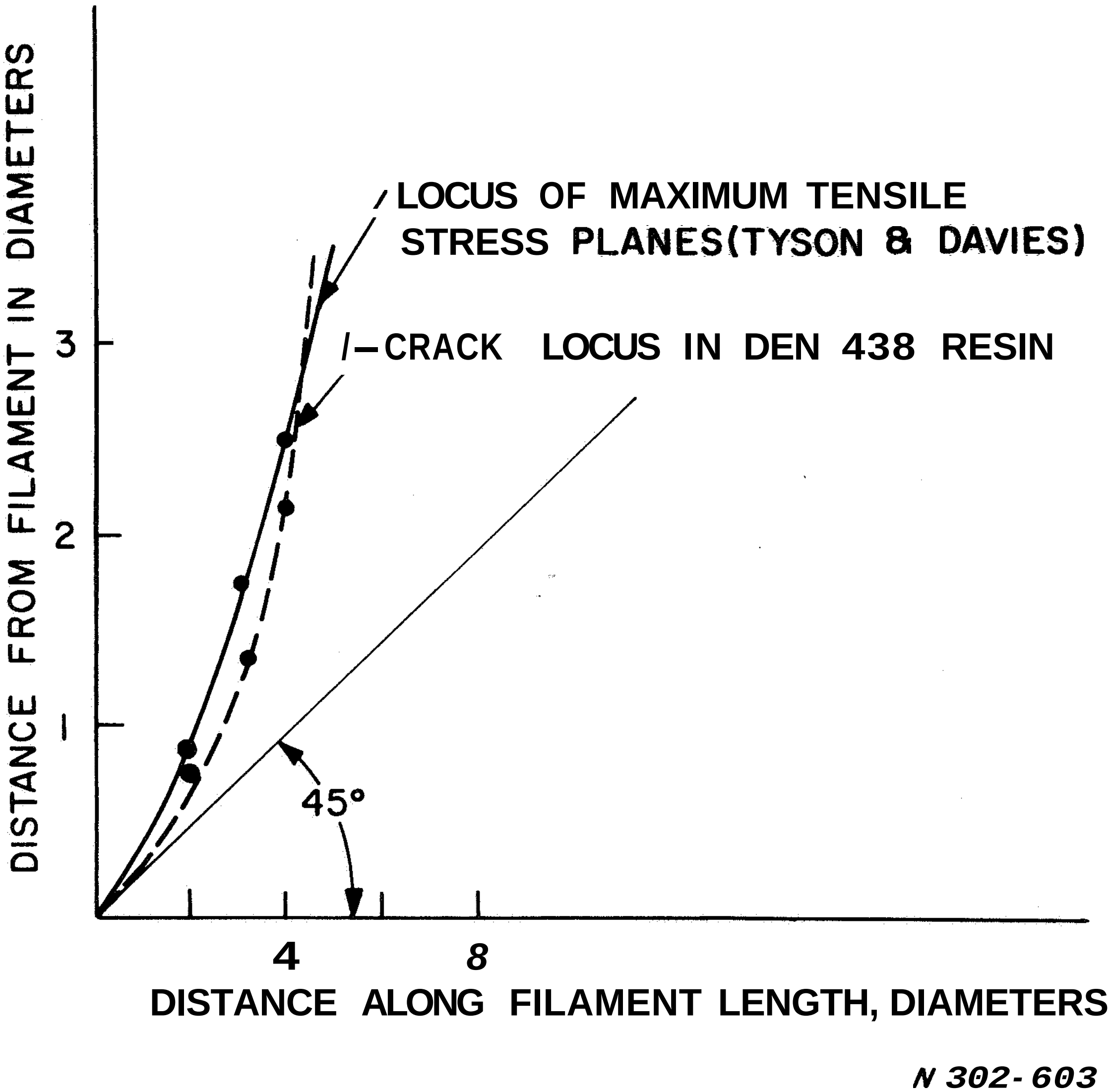


Figure 16. Plot of Locus of Crack (Fig. 15) Against Maximum Normal Stress Planes at Corresponding Distance from Filament End. Included is the Data of Tyson and Davies[8]

III. CONCLUSIONS

1. $B_4C/B/W$ continuous filaments of significant diameter (<. 004) have been produced through the deposition of B_4C on a substrate of B/W filament by the reaction BCl_3 t CH_4 t H_2 without seriously affecting the tensile strength of the starting filament in most instances.

2. It is believed that the failure of the BBr_3 t CCl_4 system to grow definitive B_4C whiskers lies in the fact that no carbon carrying species are found in the gas phase such as BC, B_2C and BC_2. These species **may** be required for whisker nucleation since these species are present when such B_4C is vaporized to produce B_4C whiskers by the method developed earlier[9]. Because of this possibility, other systems which contain B-C combinations (such as tributyl borane $(BCC_4H_9)_3$) and ethyl decaborane $(CC_2H_5B_{10}H_3)$) are presently being used as feed materials in whisker growth studies.

3. It has been established that Ti/Ni coating on $B_4C/B/W$ filaments did not affect their room temperature strength after temperatures cycling to 720°C.

4. Three modes of failure which occur in epoxy-based composites have been observed and documented. They include debonding, matrix failure at filament ends, and high speed tensile cracks which originate in the filaments and are transmitted to the matrix. Specimens frequently exhibit mixed failure modes but it is unusual **for** debonding and matrix tensile failure at filament ends to occur in the same specimen. The high speed tensile cracks can have a dynamically catastrophic effect upon nearby filaments in a multiple filament composite.

5. Preliminary experiments on epoxy B/W filaments using B/W filaments deposited under conditions which preserve the ductility of the W core show that the core can support some of the load released by the boron fracture. The differences in fracture of these composites indicate that the introduction of some ductility in a normally brittle filament may have profound effects on composite to performance.

6. A theoretical treatment of the failure modes observed in epoxy single filament composites has shown that the observations are compatible with the stress fields and shear strain models developed by others [7,8]. Experimental results agree well with theory thus it is postulated that the epoxy model can be utilized to study the fracture behavior of composite materials without fear that the epoxy system represents only a special case.

IV. FUTURE WORK

Future studies will continue to focus attention on producing $B_4C/B/W$ filament for composite studies, and additional experiments concerning production of boron carbide whiskers by chemical vapor deposition rather than by evaporation. Further studies of the fracture behavior of both single-filament and continuous filament composites in both epoxy and aluminum will be pursued to further clarify the present hypothesis of both filament and composite failure. Experimental work on achieving continuous and discontinuous reinforcement of aluminum usinp characterized Ti/Ni coated $B_4C/B/W$ filaments will be done.

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